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# Improvements in Aluminum Adhesion and Breakdown Voltages of Polyvinylidene Fluoride Films Following Exposure to Gas Plasmas

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Changes in water wettability, improvement in adhesion of vapor-deposited aluminum, and increases in dielectric breakdown voltage in thin, 12-micron Polyvinylidene fluoride (PVDF) films were observed following their brief exposure to low-temperature gas plasmas.

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## TABLE

## INTRODUCTION

Polyvinylidene fluoride (PVDF), a semicrystalline polymer with a backbone of $CH_2$-$CF_2$ repeat units, has been widely investigated and exploited as a potential dielectric film for many applications. The discovery of the combination of piezoelectric, pyroelectric, and ferroelectric properties of PVDF has generated extensive research interests. This polymer has drawn attention because of its unusually high dielectric constant, which is of interest in piezoelectric and capacitor applications, and because its electrical properties are closely related to its crystalline structure, which can be altered by poling or stretching.

Despite its interesting properties, PVDF suffers from some notable drawbacks. Aluminum does not adhere well to PVDF; it is basically a hydrophobic material. Its breakdown voltage is lower than the more traditional polymers used in capacitors, such as polypropylene and polyester. It may be easier to modify some of the surface chemical and physical properties of PVDF by changing the top few monolayers without affecting desirable bulk properties.

Among surface-modification methods, rf-activated, low-temperature, low-pressure gas plasma techniques are inexpensive and relatively easy to use, without producing severe thermal damage to bulk polymers.[1] Gas plasmas provide a rich medium of metastable, excited, reactive species (such as free radicals and ions) that react with the top few hundred angstroms of polymer surfaces to change chemical and/or morphological properties. In this report we evaluate various plasma-treatment procedures that can be applied to PVDF film prior to metallization in order to enhance the water wettability and subsequent adhesion of vapor-deposited aluminum, and increase the breakdown voltage.

## EXPERIMENTAL

Polyvinylidene film (12 microns thick) was purchased from Kureha Ltd. Coupons (5 cm X 17 cm) were cut from the roll and subjected to various plasma treatments. Unmetallized coupons were used for contact-angle and voltage-breakdown tests; adhesion was measured on films that had been metallized in a commercial metallizer by vapor deposition. Adhesion of aluminum was measured by placing a piece of 810 Scotch brand tape over metallized PVDF, removing the tape, and determining qualitatively how much aluminum was removed. A minimum of seven voltage breakdown tests were conducted on different portions of each film sample in order to obtain statistically meaningful results.

Applied voltages across the films under test were ramped at 500V /sec from zero volts until the sample underwent breakdown and did not hold off additional voltage. For ac breakdown measurements, a Hipotronics OC 60 9 (60 kV, 2 kVA) was used; a Hipotronics 260 TS (negative polarity, 60 kV, 10 mA) was used for dc breakdown measurements. Films under test were held between one-quarter inch brass electrodes while immersed in Corning 561 silicon transformer oil at room temperature. The dielectric constant of the oil at one kilohertz was 2.75, with a dissipation factor of $1 \times 10^{-5}$.

Polyvinylidene samples were treated with various gas plasmas by placing them in a Branson/IPC (Fort Washington, PA) Model 7104 plasma etcher for four minutes at 250 watts, a gas pressure of 150 torr, and a gas flow rate of 0.3 ml per minute. Based on the chamber volume, the power density was 0.002 watts/cm$^3$. We studied three separate gases: oxygen, helium, and a mixture of $96\%CF_4/4\%O_2$. Chamber temperatures did not increase substantially following the plasma treatments.

RESULTS AND DISCUSSION

Table 1 summarizes our experimental results. There is poor adhesion of vapor-deposited aluminum to PVDF that had not been exposed to gas plasma. Cleaning untreated PVDF film with methylene chloride (to remove dirt) prior to metallization did not improve aluminum adhesion. Excellent aluminum adhesion was found for PVDF treated with any of the three gas plasmas studied. The contact angle of water on PVDF decreased sharply following exposure to $O_2$ plasma; the decrease was less dramatic for PVDF exposed to the other two gas plasmas. Increased wettability (lower contact angle) implies that the hydrophobic nature of the PVDF surface was reduced greatly. Table 1 also shows the average (top number) and 90 percent confidence limits (number range within parentheses), based on Weibull statistics of breakdown voltages $V_b$ for both dc and ac voltages, for films that had been exposed to each of the three gas plasmas. Polyvinylidine fluoride that had been exposed to oxygen showed a 26 percent increase in ac $V_b$; PVDF exposed to $96\%CF_4/4\%O_2$ plasma showed an 11 percent improvement in dc $V_b$.

We could speculate on the reasons for the observed changes in contact angle and adhesion of aluminum and $V_b$ for some of these PVDF samples. One possible reason for the changes could be that exposure to the gas plasma (and subsequently the atmosphere) formed a chemically modified, hydrophillic surface region to which aluminum adheres well, and which impedes injected charge

TABLE 1. Various properties of 12 micron-thick PVDF films that had been exposed to either oxygen, helium or 96%$CF_4$/4%$O_2$ gas plasmas. Properties include: contact angle of water (in degrees), relative adhesion of vapor-deposited aluminum (described as either excellent or poor), and dc and ac breakdown voltages (in kilovolts). The ac values are root mean square values.

| Plasma treatment | Contact angle, degrees | Aluminum adhesion | ac $V_b$ | dc $V_b$ |
|---|---|---|---|---|
| - | 71 | poor | 2.70<br>(2.63-2.77) | 7.19<br>(6.79-7.63) |
| oxygen | 40 | excellent | 3.42<br>(2.78-4.30) | 7.58<br>(7.15-8.07) |
| helium | 57 | excellent | 2.76<br>(2.70-2.82) | 7.72<br>(7.07-8.46) |
| 96%$CF_4$/4%$O_2$ | 70 | excellent | 2.75<br>(2.70-2.80) | 7.96<br>(7.42-8.86) |

into the bulk. This could decrease electric field strengths at high field points and prevent breakdown by decreasing conduction currents. Exposure of PVDF to 96% $CF_4$/4% $O_2$ plasma, for example, may be replacing hydrogen atoms with fluorine atoms and forming a modified, highly resistive, Teflon-like region near the surface, which inhibits charge injection and thereby prevents breakdown from taking place. This argument is somewhat supported by the premise that the contact angle decreases the least following $CF_4/O_2$ treatment. This would be consistent with forming a TFE-like hydrophobic region near the surface. This hypothesis is not unreasonable, since high field currents in poly-P-xylylene thin films have been suppressed by the introduction[2] of an oxidized layer on the surface which also increased $V_b$.

Possibly, the exact amount of gas-plasma treatment required for improving the adhesion, wettability, or $V_b$ can be optimized further by varying the power density, temperature, or total time in the gas-plasma chamber.

## SUMMARY

Improvements in adhesion of vapor-deposited aluminum, changes in contact angle of water, and improvements in dielectric voltage breakdown values were observed for PVDF films following exposure to various low-temperature gas plasmas.

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